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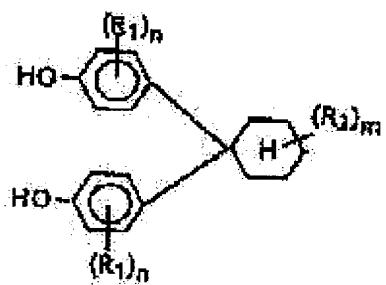
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(54) POSITIVE TYPE PHOTOSENSITIVE COMPOSITION FOR PRINTING PLATE

(57)Abstract:

PURPOSE: To obtain a positive type photosensitive composition for the printing plate capable of enhancing sensitivity without adversely affecting important characteristics such as development allowance by incorporating a specified additive.

CONSTITUTION: This positive type photosensitive composition for the printing plate contains an o-quinonediazido compound or a diazonium salt, and further the compound represented by formula I in which each of R1 is H, OH, halogen, alkyl, alkoxy, alkenyl, aryl, aralkyl, arylcarbonyl, acyloxy, acyl, or aroxy; R2 is H, halogen, hydroxy, alkyl, or carboxy, each



independent of each other; and each of (m) and (n) is an integer between 1 and 4.

LEGAL STATUS

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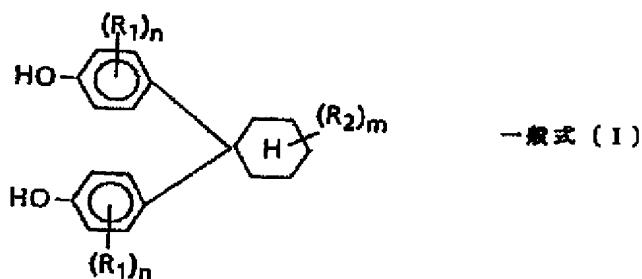
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CLAIMS

[Claim(s)]

[Claim 1] The positive type photosensitivity constituent for the printing versions
characterized by containing the compound shown by the following general formula (I)
in the positive type photosensitivity constituent for the printing versions containing
o-quinone diazide compound or diazonium salt.

[Formula 1]



R1 expresses a hydrogen atom, a hydroxyl group, a halogen atom, an alkyl group, an alkoxy group, an alkenyl radical, an aryl group, an aryl carbonyl group, an acyloxy radical, an acetoxy radical, an acyl group, or an AROKISHIRU radical, and R2 expresses a hydrogen atom, a halogen atom, a hydroxyl group, an alkyl group, or a carboxyl group here, and even if the same, you may differ. m expresses the integer of 1-4 and n expresses the integer of 1-4.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the positive type photosensitivity constituent for the printing versions which added and high-sensitivity-ized the specific compound to the positive type photosensitivity constituent for the printing versions which comes to contain o-quinone diazide compound or diazonium salt especially about the lithography version and the positive type photosensitivity constituent for the printing versions suitable for manufacture of proofreading printing of process printing. Furthermore, it is related with the positive type photosensitivity constituent for the printing versions which can raise sensibility in detail, without affecting development admissibility.

[0002]

[Description of the Prior Art] Conventionally, in the application of the lithography version, what prepared the photosensitive constituent which various proposals are performed as the so-called photosensitive constituent which is solubilized with an activity beam of light, and which acts positively, for example, contains o-quinone diazide compound on an aluminum substrate, or the photosensitive constituent containing diazonium salt is known. o-quinone diazide compound is a photosensitive compound of the positive type studied most, decomposition is caused by the exposure

of an activity beam of light, the carboxylic acid of five membered-rings is produced, and becoming meltable at an alkali water solution is known. As such an o-quinone diazide compound for example, U.S. Pat. No. 2,766,118 -- said -- the 2,767,092nd a number -- said -- the 2,772,972nd a number -- said -- the 2,859,112nd a number -- said -- the 2,907,665th a number -- said -- the 3,046,110th a number -- said -- the 3,046,111st a number -- said -- the 3,046,115th a number -- said -- the 3,046,118th a number -- said -- the 3,046,119th a number -- said -- the 3,046,120th a number -- said -- the 3,046,121st a number -- said -- the 3,046,122nd a number -- said -- the 3,046,123rd a number -- said -- the 3,061,430th a number and 3,102,809 -- said -- the 3,106,465th a number -- said -- the 3,635,709th a number -- said -- the 3,647,443rd Each description of a number is begun and it is describing in many periodicals. Although the image quality of a good positive type could be formed by using these compounds, photochemistry-[o-quinone diazide compound]-on the other hand sensitization was difficult, and in order that a quantum yield might not exceed 1 in essence, it was not what all shows sufficient sensibility. What is satisfied is not obtained although various proposals have been conventionally made about the approach of raising the positive type photosensitivity of this o-quinone diazide system. For example, seemingly, when the amount of o-quinone diazide compound is lessened, although sensibility rises, it follows on it, the development admissibility at the time of development (time amount width of face by which the optimal development result is permitted by being obtained) becomes narrow, and it is lacking in practicability.

[0003] Moreover, the system which combined the large binder resin of alkali water-solution solubility with o-quinone diazide compound gives the same result as the above. Moreover, although some techniques of adding a nonphotosensitivity compound (sensitizer) to the photosensitive constituent containing o-quinone diazide compound, and raising sensibility are proposed, the actual condition is neither acquiring sufficient effectiveness and having various faults. For example, although sensibility could be raised by addition of a fixed heterocyclic compound, for example, 2-azacyclo NANON-2-ON, Indore, quinazoline, and tetrazole as indicated by the U.S. Pat. No. 3,661,582 description, it had narrow development admissibility in the degree of pole like the case where it describes above also in this case. Furthermore, although the additives, for example, the triphenylmethane dye, the benzaldehyde-m-tolyl hydrazines, the various halogenated hydrocarbon, and various azo dye for raising photographic sensitivity are indicated by JP,46-42449,B, these compounds do not have remarkable high sensitivity-sized effectiveness.

[0004] Moreover, for the same object, o-benzoic-acid sulfimide, hydantoin and its

derivative, thiohydantoin, and its derivative are proposed by JP,50-36203,A, and the additive of an acid anhydride is proposed by JP,52-80022,A. However, it set to the addition which is extent lifting of sensibility is accepted to be also in these cases, and there was a fault to which the development admissibility at the time of development becomes narrow. Furthermore, although addition of the condensation product of a hydroxy benzophenone and formaldehyde was proposed for the purpose of sensibility lifting by JP,55-73045,A, an addition remarkable for accepting needs distinct sensibility lifting, and lowering of development admissibility and chemical resistance was not able to be escaped. Furthermore, although several sorts of compounds are indicated by JP,57-118237,A and JP,57-118238,A for the object of high-sensitivity-izing, it has the fault in development admissibility. as the positive setup-of-tooling product which contains diazonium salt on the other hand -- U.S. Pat. No. 3,219,447 -- said -- the 3,211,553rd Although what is indicated by a number, JP,39-7663,B, JP,52-2519,A, etc. was raised, it was low sensibility, and since the stability of image formation was missing, practical use was not able to be presented. Although addition was tried for the compound of a publication for the purpose of high-sensitivity-izing to these photosensitive constituents at U.S. Pat. No. 3,661,582 and JP,52-80022,A, high-sensitivity-izing and development admissibility were not able to be reconciled like the positive type photo conductor of o-quinone diazide system.

[0005]

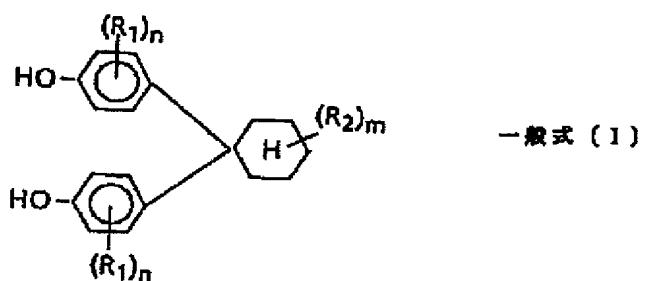
[Problem(s) to be Solved by the Invention] The object of this invention is to offer the positive type photosensitivity constituent for the printing versions which can raise sensibility, without having disadvantageous effect for other important properties, such as development admissibility, by making a specific additive contain.

[0006]

[Means for Solving the Problem] By making the compound shown in the positive type photosensitivity constituent for the printing versions containing o-quinone diazide compound or diazonium salt by the following general formula (I) contain, this invention person found out that the above-mentioned object was attained.

[0007]

[Formula 2]



[0008] R1 expresses a hydrogen atom, a hydroxyl group, a halogen atom, an alkyl group, an alkoxy group, an alkenyl radical, an aryl group, an aryl carbonyl group, an acyloxy radical, an acetoxy radical, an acyl group, or an AROKISHIRU radical, and R2 expresses a hydrogen atom, a halogen atom, a hydroxyl group, an alkyl group, or a carboxyl group here, and even if the same, you may differ. m expresses the integer of 1–4 and n expresses the integer of 1–4. The positive type photosensitivity constituent for the printing versions of this invention is explained to a detail below. The positive type photosensitivity constituent for the printing versions of this invention prepares the photosensitive constituent of the positive type containing o-quinone diazide compound or diazonium salt on a base material, and prepares a mat layer for undercoat on a photosensitive constituent layer between them if needed.

[0009] As a base material used for this invention, it is a tabular object stable in dimension. for example, paper and plastics (for example, polyethylene and polypropylene --) the paper which polystyrene etc. laminated, and a metal plate (for example, aluminum --) plastic films (for example, diacetyl cellulose --), such as zinc and copper A cellulose triacetate, cellulose propionate, a butanoic acid cellulose, a cellulose acetate butyrate, The paper in which the metal like the above, such as a cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, a polycarbonate, and a polyvinyl acetal, was laminated or vapor-deposited, or a plastic film is contained. Also in it, dimensional stability is good and especially a comparatively cheap aluminum plate has it. [desirable] A suitable aluminum plate may be an alloy plate which uses a pure aluminium plate and aluminum as a principal component, and contains the different element of a minute amount, and the plastic film with which aluminum was laminated or vapor-deposited further is sufficient as it. There are silicon, iron, manganese, copper, magnesium, chromium, zinc, a bismuth, nickel, titanium, etc. in the different element contained in an aluminum alloy. The content of the different element in an alloy is at most 10 or less % of the weight. Although especially suitable aluminum is pure aluminium in this invention, since manufacture on a refining technique is difficult for completely pure aluminum, a different element may

be contained slightly. Thus, the presentation is not specified and the aluminum plate of the raw material of well-known official business can be conventionally used for the aluminum plate applied to this invention suitably. The thickness of the aluminum plate used by this invention is about 0.1mm – about 0.6mm. It precedes carrying out surface roughening of the aluminum plate, and cleaning processing by the surfactant, the organic solvent, or the alkaline water solution in order for a request to remove surface rolling oil is performed.

[0010] Although the surface roughening process of the front face of an aluminum plate is performed by various approaches, it is performed by the approach of carrying out surface roughening mechanically, for example, the approach of carrying out dissolution surface roughening of the front face electrochemically, and the approach of carrying out selective dissolution of the front face chemically. As the mechanical approach, well-known approaches, such as the ball grinding method, a brushing method, the blasting grinding method, and buffing, can be used. Moreover, there is the approach of performing according to an alternating current or a direct current in a hydrochloric acid or the nitric-acid electrolytic solution as an electrochemical surface roughening method. Moreover, the approach which combined both as indicated by JP,54-63902,A can also be used. Thus, anodizing is performed in order that the aluminum plate by which surface roughening was carried out may raise surface water retention and abrasion resistance by request, after alkali-etching-processing and neutralization processing if needed. As an electrolyte used for anodizing of an aluminum plate, the activity of the various electrolytes which form a porosity oxide film is possible, and, generally a sulfuric acid, a phosphoric acid, oxalic acid, chromic acids, or those mixed acids are used. The concentration of those electrolytes is suitably decided according to an electrolytic class. Since the processing conditions of anodic oxidation change variously with the electrolyte to be used, it cannot generally specify, but generally, if electrolytic concentration is 5–70 degrees C, current density 5 – 60 A/dm², electrical potential differences 1–100V, and the range for 10 seconds – electrolysis time amount 5 minutes, it is suitable for a 1 – 80-% of the weight solution, and solution temperature. If there are few amounts of an anodic oxide film than 1.0 g/m², its print durability is inadequate, or the so-called “blemish dirt” with which a blemish becomes easy to stick to the non-image section of the lithography version with, and ink adheres to the part of a blemish at the time of printing becomes easy to produce them. After anodizing is performed, as for an aluminum front face, hydrophilization processing is performed as occasion demands. as the hydrophilization processing used for this invention -- U.S. Pat. No. 2,714,066 -- said -- the

3,181,461st A number and the 3,280,734th A number and the 3,902,734th alkali-metal silicate (for example, sodium-silicate water solution) which is indicated by the number -- there is law. or [that immersion processing of the base material is carried out in a sodium-silicate water solution in this approach] -- or electrolysis processing is carried out. the fluoride zirconic acid potassium currently otherwise indicated by JP,36-22063,B and U.S. Pat. No. 3,276,868 -- said -- the 4,153,461st a number -- said -- the 4,689,272nd The approach of processing by polyvinyl phosphonic acid which is indicated by the number etc. is used.

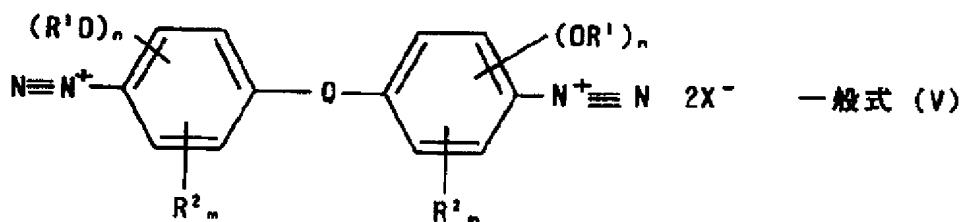
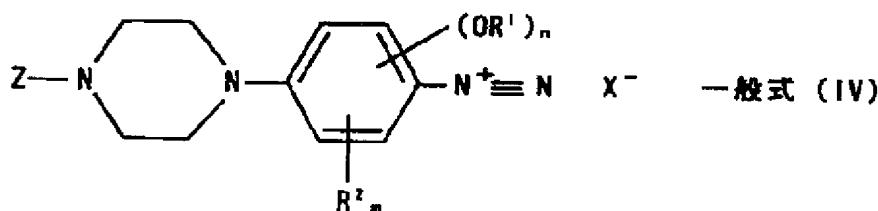
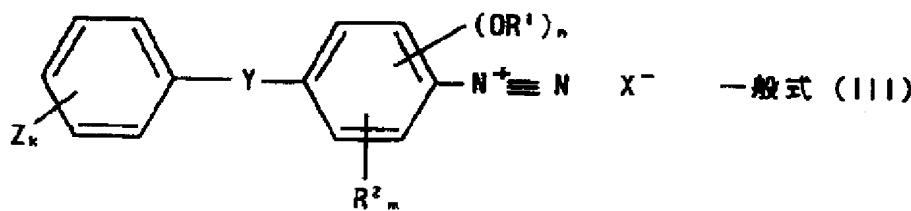
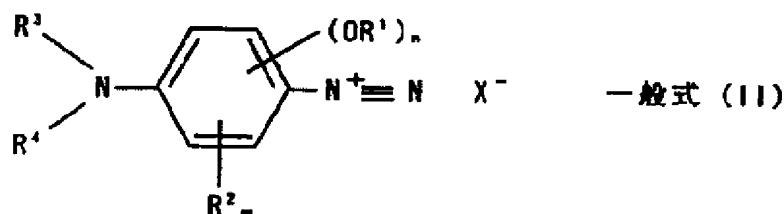
[0011] Next, the positive type photosensitivity constituent with which the compound shown by the above-mentioned general formula (I) is added is explained. The photosensitive constituent which contains o-quinone diazide compound or diazonium salt better known than before as a positive type photosensitivity constituent can be used. Although these photosensitive constituents mainly consist of o-quinone diazide compound or diazonium salt, and an alkali fusibility binder, the case where especially an alkali fusibility binder is phenol nature resin is desirable. o-quinone diazide compound used for this invention is a compound which has at least one o-quinone diazide radical, it increases alkali fusibility by activity beam-of-light exposure, and the compound of various structures can be used for it. for example, J. Koser work "light-sensitive systems" (John Wiley & Sons.Inc.) -- although the compound of a publication can be used [page / 339-352nd], various aromatic series polyhydroxy compounds or the aromatic series amino compound, the sulfonate of o-quinone diazide made to react, or a sulfonic-acid amide is especially suitable. moreover, the ester of benzoquinone-(1 2)-diazido sulfonic-acid chloride or naphthoquinone-(1 2)-diazido sulfonic-acid chloride, and pyrogallol-acetone resin which are indicated by JP,43-28403,B and U.S. Pat. No. 3,046,120 -- and -- said -- the 3,188,210th The ester of the benzoquinone-(1 2)-diazido sulfonic-acid chloride or naphthoquinone-(1 2)-diazido sulfonic-acid chloride, and phenol-formaldehyde resin which are indicated by the number is also used suitably. As other useful o-quinone diazide compounds, it is reported to much patents and known. For example, JP,47-5303,A, JP,48-63802,A, JP,48-63803,A, JP,48-96575,A, JP,49-38701,A, JP,48-13354,A, JP,41-11222,B, JP,45-9610,B, JP,49-17481,B, U.S. Pat. No. 2,797,213 -- said -- the 3,454,400th a number -- said -- the 3,544,323rd a number -- said -- the 3,573,917th a number -- said -- the 3,674,495th a number -- said -- the 3,785,825th A number and British patent 1,227,602nd a number -- said -- the 1,251,345th a number -- said -- the 1,267,005th a number -- said -- the 1,329,888th a number -- said -- the 1,330,932nd A number and German patent 854,890th What is indicated in each description, such as

a number, can be raised.

[0012] moreover --- as the diazonium salt used by this invention --- U.S. Pat. No. 3,219,447 --- said --- the 3,211,553rd The well-known diazonium salt of a publication can be raised to a number, JP,39-7663,B, JP,52-2519,A, Japanese Patent Application No. No. 325859 [three to], etc. Although the compound especially shown as an example of effective diazonium salt by the following general formula (II), (III), (IV), and (V) can be mentioned, it is not limited to this.

[0013]

[Formula 3]



[0014] Inside R1 of a formula The alkyl group or permutation alkyl group of carbon

numbers 3–18 is shown, and it is R2. A hydrogen atom, an alkyl group, a permutation alkyl group, an aryl group, a permutation aryl group, an alkoxy group, a permutation alkoxy group, a phenoxy group, a permutation phenoxy group, or a halogen atom is shown. X – A pair anion is shown. n shows the integer of 1–4, m shows the integer of 1–3, and it is $n+m=4$. R3 and R4 An alkyl group, a permutation alkyl group, an aryl group, or a permutation aryl group is shown independently respectively. Moreover, R3 R4 It may join together mutually and heterocycle type machines, such as a morpholino radical, a piperidino radical, a piperazinyl radical, and a pyrrolidinyl radical, may be formed. Y shows an oxygen atom, a sulfur atom, $-NH-$, $-CH_2-$, or $-C(CH_3)_2-$. Z shows a hydrogen atom, an alkyl group, a permutation alkyl group, an aryl group, a permutation aryl group, an alkoxy group, a permutation alkoxy group, an alkyl carbonyl group, a permutation alkyl carbonyl group, an aryl carbonyl group, a permutation aryl carbonyl group, a cyano group, a nitro group, or a halogen atom. k shows the integer of 1–5. Q shows the connection radical of bivalence.

[0015] The addition of o-quinone diazide compound used by this invention or diazonium salt is 5 – 30% of the weight of the range still more preferably one to 50% of the weight to photosensitive constituent total solids preferably. Although these compounds are single and it can be used, you may use it as several sorts of mixture. As an alkali fusibility binder used by this invention, they are pKall(s), such as a phenol nature hydroxy group, a carboxylic-acid radical, a sulfonic group, an imide radical, a sulfonamide radical, N-sulfonyl amide group, N-sulfonyl urethane group, and an activity methylene group, preferably. It is the polymer which has the following acidic groups. As a suitable alkali fusibility polymer, phenol-formaldehyde resin, o-cresol formaldehyde resin, m-cresol formaldehyde resin, p-cresol-formaldehyde resins, xylenol-formaldehyde resins, or these copolycondensation objects are in novolak mold phenol resin and a concrete target. Furthermore, the condensate of the phenol or cresol permuted with the above phenol resin by the alkyl group of carbon numbers 3–8 like t-butylphenol-formaldehyde resins as described at JP,50-125806,A, and formaldehyde may be used together. Moreover, independent or copolymerization polymers, such as N-hydroxystyrene, m-isopropenyl phenol, and p-isopropenyl phenol, and the polymer in which these polymers carried out part etherification or partial esterification further can also be used. Furthermore, the polymer which uses carboxy group content monomers, such as an acrylic acid and a methacrylic acid, as a copolymerization component, carboxy group content polyvinyl-acetal resin given in JP,61-267042,A, and carboxyl group content polyurethane resin given in JP,63-124047,A are also used suitably. Furthermore, the polymer and the activity

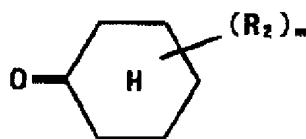
methylene group content polymer given in JP,63-127239,A which use N-(4-sulfamoyl phenyl) methacrylamide, N-phenyl sulfonyl methacrylamide, and maleimide as a copolymerization component can also be used again. Although these alkali fusibility polymers are single and it can be used, you may use it as several sorts of mixture. The addition of the alkali fusibility polymer under sensitization object presentation is 10 – 90% of the weight of the range still more preferably five to 99% of the weight to sensitization object presentation total solids preferably.

[0016] Next, the compound shown by the general formula (I) is explained. By adding to the photosensitive constituent of a positive type, the compound shown by the general formula (I) can raise sensibility, without having disadvantageous effect for other important properties, such as development admissibility. In R1 and R4 of the above-mentioned general formula (I) as a halogen atom A chlorine atom, a bromine atom, or an iodine atom as an alkyl group A methyl group. The alkyl group of carbon numbers 1–4 like an ethyl group, a propyl group, n-butyl, an isobutyl radical, sec-butyl, or t-butyl. The alkoxy group of carbon numbers 1–4 like a methoxy group, an ethoxy radical, a hydroxy ethoxy radical, a propoxy group, a hydroxy propoxy group, an isopropoxy group, an n-butoxy radical, an iso-butoxy radical, a sec-butoxy radical, or a t-butoxy radical as an alkoxy group is desirable. As an alkenyl radical, a vinyl group, a propenyl radical, an allyl group, or the alkenyl radical of carbon numbers 2–4 like a butenyl group is desirable. As an aryl group, a phenyl group, a xylyl group, a toluyl radical, a KUMENIRU radical, As an aralkyl radical, benzyl, a phenethyl radical, and a cumyl radical as an alkoxy carbonyl group A methoxycarbonyl group, An ethoxycarbonyl radical as an aryl carbonyl group a benzyloxy radical as an acyloxy radical — a butyryloxy radical and an acetoxy radical — as an AROKISHIRU radical, a benzyloxy radical has [a formyl group, an acetyl group, a butyryl radical, benzoyl, a SHIANA moi radical, and a valeryl radical] a phenoxy group desirable as an acyl group as an aralkoxy radical.

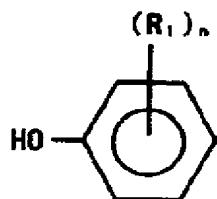
[0017] The compound expressed with a general formula (I) is obtained by the approach given in JP,63-10745,A, 63-41433, 64-25746, 64-26533, 64-63547, 64-63548, 64-79136, JP,1-160930,A, a 1-160932 official report, etc. For example, the compound expressed with a general formula (I) is a general formula (VI). It is obtained by making the phenols expressed with the cyclohexanones expressed and a general formula (VII) react under existence of an acid catalyst.

[0018]

[Formula 4]



一般式 (VI)



一般式 (VII)

[0019] (R1 and R2 are as having given the definition previously among a formula.) General formula (VI) As a catalyst which can be used for a reaction with the compound of a general formula (VII), hydrogen chloride gas, a hydrochloric acid, a sulfuric acid, phosphoric acid, toluenesulfonic acid, BF₃, ZnCl₂, AlCl₃, SnCl₄, the cation exchange resin that has a migration acidic group are mentioned. The amount of these catalysts used is a formula (VI). It is the range per [0.1] compound 100 weight section – of 30 weight sections. Moreover, it is also possible to raise a reaction rate by addition of a co-catalyst. As an activity co-catalyst, methyl mercaptan, ethyl mercaptan, n propyl mercaptan, an isopropyl mercaptan, n-butyl mercaptan, an isobutyl mercaptan, the alkyl mercaptan like t-butyl mercaptan, or macromolecule alkyl mercaptan can be mentioned. Furthermore, other sulfur compounds like a hydrogen sulfide, a thiophenol, a thioalcohol, a thiosulfuric acid, a polymer thio acetone, and a dialkyl sulfide and the selenium compound of these resemblances can also be used. In the above-mentioned reaction, the amount of the phenols used of a formula (VII) has 10 desirable weight sections from 2 weight sections per cyclohexanones 1 weight section of a formula (VI). reaction temperature -- the range of 30–100 degrees C — it is the range of 40–70 degrees C preferably. Since a by-product will increase and yield will fall if reaction temperature is too high, it is not desirable.

[0020] thus, as an example of a compound expressed with the general formula (I) obtained 4 and 4'-bis(4-hydroxyphenyl)-cyclohexane carboxylic acid, 4 and 4'-bis(3-tert-butyl-4-hydroxyphenyl)-cyclohexane carboxylic acid, 2 and 2'-bis(4-hydroxyphenyl)-cyclohexane carboxylic acid, A 2 and 2'-bis(4-hydroxyphenyl)-3-methylcyclohexane carboxylic acid, A 2 and 2-bis(4-hydroxyphenyl)-4-methylcyclohexane carboxylic acid, A 2 and

2-bis(4-hydroxyphenyl)-5-methylcyclohexane carboxylic acid, A 2 and
2-bis(4-hydroxyphenyl)-6-methylcyclohexane carboxylic acid, A 2 and
2-bis(4-hydroxyphenyl)-3-ethylcyclohexane carboxylic acid, A 2 and
2-bis(4-hydroxyphenyl)-4-ethylcyclohexane carboxylic acid, A 2 and
2-bis(4-hydroxyphenyl)-5-ethylcyclohexane carboxylic acid, A 2 and
2-bis(4-hydroxyphenyl)-6-ethylcyclohexane carboxylic acid, The 2 and 2-screw
(4-hydroxyphenyl) -3, 4-dimethylcyclohexane carboxylic acid, The 2 and 2-screw
(4-hydroxyphenyl) -3, 5-dimethylcyclohexane carboxylic acid, The 2 and 2-screw
(4-hydroxyphenyl) -3, 6-dimethylcyclohexane carboxylic acid, The 2 and 2-screw
(4-hydroxyphenyl) -4, 5-dimethylcyclohexane carboxylic acid, The 2 and 2-screw
(4-hydroxyphenyl) -5, 6-dimethylcyclohexane carboxylic acid, 2 and
2-bis(4-hydroxy-2-methylphenyl)-cyclohexane carboxylic acid, 2 and
2-bis(4-hydroxy-3-methylphenyl)-cyclohexane carboxylic acid, 2 and
2-bis(4-hydroxy - 3, 5-dimethylphenyl)-cyclohexane carboxylic acid, A 2 and
2-bis(4-hydroxy - 3, 5-dimethylphenyl)-4-methylcyclohexane carboxylic acid, A 2 and
2-bis(4-hydroxy - 3, 5-dimethylphenyl)-5-methylcyclohexane carboxylic acid, A 1
and 1-bis(4-hydroxyphenyl) cyclohexane, 4-methyl -1, 1-bis(4-hydroxyphenyl)
cyclohexane, 3, and 3-bis(4-hydroxyphenyl) cyclohexanol etc. can be mentioned.

[0021] These compounds are independent or are used in two or more sorts of combination. The loadings of the compound expressed with a general formula (I) are usually the 5 - 100 weight section preferably below the 150 weight sections to the quinone diazide compound 100 weight section. If the sensibility lifting effectiveness is not substantially acquired for this rate of an use rate under in 5 weight sections and the 150 weight sections are exceeded, a remaining rate of membrane will fall remarkably. To the positive type photosensitivity constituent for the printing versions of this invention, various additives can be added further if needed. For example, it is desirable to use together the condensate of the phenol which has the alkyl group of carbon numbers 3-8 like octyl phenol formaldehyde resins as a substituent, and formaldehyde, when raising the admiration oily skin of an image.

[0022] Moreover, cyclic anhydrides, phenols, and organic acids can also be made to use together in order to raise sensibility further. The phthalic anhydride indicated by the U.S. Pat. No. 4,115,128 description as a cyclic anhydride, tetrahydro phthalic anhydride, hexahydro phthalic anhydride, 3, 6-ENTO oxy—delta4-tetrahydro phthalic anhydride, tetra-KURORU phthalic anhydride, a maleic anhydride, the Krol maleic anhydride, alpha-phenyl maleic anhydride, a succinic anhydride, pyromellitic dianhydride, etc. can be used. phenols -- ***** -- bisphenol A -- p - a nitrophenol

— p — ethoxy — a phenol — two — four — four — ' — trihydroxy — a benzophenone — two — three — four — trihydroxy — a benzophenone — four — hydroxy one — a benzophenone — four — four — ' — four — " — trihydroxy — a triphenylmethane color — four — four — ' — three — " — four — " — tetra — hydroxy one — 3, 5, 3', and 5' — tetramethyl triphenylmethane color etc. is mentioned. Furthermore, are indicated by JP,60-88942,A, JP,2-96755,A, etc. as organic acids. There are sulfonic acids, sulfinic acids, alkyl sulfuric acid, phosphonic acid, phosphoric ester, and carboxylic acids. Specifically P-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluene sulfinic acid, Ethyl sulfuric acid, phenylphosphonic acid, phenyl phosphinic acid, phosphoric-acid phenyl, Phosphoric-acid diphenyl, a benzoic acid, isophthalic acid, an adipic acid, para toluyllic acid, 3, 4-dimethoxy benzoic acid, a phthalic acid, a terephthalic acid, 1, the 4-cyclohexene-2, 2-dicarboxylic acid, an erucic acid, a lauric acid, an n undecane acid, an ascorbic acid, etc. are mentioned. The rate of occupying in the photosensitive constituent of the above-mentioned cyclic anhydride, phenols, and organic acids has 0.05 — 15 desirable % of the weight, and it is 0.1 — 5 % of the weight more preferably.

[0023] Moreover, in order to extend the stability of the processing to development conditions in the photosensitive constituent in this invention, they are JP,62-251740,A and Japanese Patent Application No. 2-188. A nonionic surface active agent which is indicated by the number description, JP,59-121044,A, and an amphoteric surface active agent which is indicated by the Japanese-Patent-Application-No. No. 115992 [two to] description can be added. As an example of a nonionic surface active agent, sorbitan tris TEARITO, sorbitan monopalmitate, a sorbitan trio rate, a stearin acid monoglyceride, the polyoxyethylene nonylphenyl ether, etc. are mentioned. As an example of a double-sided activator, alkyl di(aminoethyl)glycine, an alkylpolyamino ethylglycine hydrochloride, 2-alkyl-N-carboxy ethyl-N-hydroxyethyl imidazolinium betaine, N-tetradecyl-N and N-betaine mold (for example, trade name Amogen K, the product made from the first Industry), etc. are mentioned. The rate of occupying in the photosensitive constituent of the above-mentioned nonionic surface active agent and an amphoteric surface active agent has 0.05 — 15 desirable % of the weight, and it is 0.1 — 5 % of the weight more preferably. Into the photosensitive constituent in this invention, the color and pigment as the baked appearance electuarium and the image coloring agent for obtaining a visible image promptly after exposure can be added. As baked appearance electuarium, the combination of the compound (photo-oxide bleedoff agent) which emits an acid by exposure, and the organic dye which can form a salt can be

mentioned as a representative. the combination of o-naphthoquinonediazide-4-sulfonic-acid halo GENIDO specifically indicated by each official report of JP,50-36209,A and 53-8128, and salt plasticity organic dye, and JP,53-36223,A -- said -- 54-74728 a number, 60-3626, 61-143748, and 61-151644 -- and -- said -- 63-58440 The combination of the trihalomethyl compound indicated by each official report of a number and salt plasticity organic dye can be mentioned. as this trihalomethyl compound, there are an oxazole system compound and triazine compound, and it passes through both, excels in the Tokiyasu quality, and clear -- appearance is burned and carried out and an image is given.

[0024] As a coloring agent of an image, other colors can be used in addition to the above-mentioned salt plasticity organic dye. An oil color and basic dye can be raised as a suitable color also including salt plasticity organic dye. Specifically, oil yellow #101, oil yellow #103, oil pink #312, the oil green BG, oil blue BOS, oil blue #603, oil black BY, oil black BS, oil black T-505 (above product made from ORIENT Chemical industry), Victoria pure blue, a crystal violet (CI42555), Methyl Violet (CI42535), ethyl violet, rhodamine B (CI145170B), Malachite Green (CI42000), a methylene blue (CI52015), etc. can be mentioned. Moreover, especially the color indicated by JP,62-293247,A is desirable. These colors can be preferably added in a photosensitive constituent at 0.1 – 3% of the weight of a rate 0.01 to 10% of the weight to photosensitive constituent total solids. Furthermore, a plasticizer is added in order to give the flexibility of a paint film etc. if needed into the photosensitive constituent of this invention. For example, oligomer, a polymer, etc. of butyl phthalyl, a polyethylene glycol, tributyl citrate, a diethyl phthalate, dibutyl phtalate, phthalic-acid dihexyl, a dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, an acrylic acid, or methacrylic acid are used. The positive type photosensitivity constituent for the printing versions of this invention usually melts each above-mentioned component to a solvent, and applies it on a base material. As a solvent used here, although ethylene dichloride, cyclohexanone, methyl-ethyl-ketone, methanol, ethanol, propanol, ethylene-glycol-monomethyl-ether, 2-methoxy ethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N, and N-dimethoxy acetamide, N,N-dimethylformamide, tetramethyl urea, N-methyl pyrrolidone, dimethyl sulfoxide, a sulfolane, gamma-butyl lactone, toluene, etc. can be raised, it is not limited to this.

[0025] these solvents are independent -- or it is mixed and used. The concentration of the above-mentioned component in a solvent (total solids containing an additive) is

1 – 50 % of the weight preferably. Moreover, although the coverage on the base material obtained after spreading and desiccation (solid content) changes with applications, speaking of the photosensitive printing version, generally, 0.5 – 5.0 g/m² is desirable [coverage]. As an approach of applying, although various approaches can be used, bar coating—machine spreading, revolution spreading, spray spreading, curtain spreading, DIP spreading, the Ayr knife spreading, blade spreading, roll coating, etc. can be mentioned, for example. Although apparent sensibility becomes size as coverage decreases, the coat property of a film falls. Although the printing version using the positive type photosensitivity constituent for the printing versions of this invention prepares the photosensitive constituent of the positive type containing o-quinone diazide compound or diazonium salt on a base material, it can prepare a mat layer for undercoat on a photosensitive constituent layer between them if needed. Various organic compounds are used as an undercoat component. For example, a carboxymethyl cellulose, The phosphonic acid which has amino groups, such as a dextrin, gum arabic, and 2-aminoethylphosphonic acid The phenylphosphonic acid and naphthyl phosphonic acid which may have a substituent, alkyl phosphonic acid glycero phosphonic acid, Organic phosphonic acid, such as methylene diphosphonic acid and ethylene diphosphonic acid, Organic phosphoric acids, such as a phenyl phosphoric acid which may have a substituent, a naphthyl phosphoric acid, an alkyl phosphoric acid, and glycerophosphoric acid, Phenyl phosphinic acid, naphthyl phosphinic acid which may have a substituent, Although chosen out of the hydrochloride of the amine which has hydroxy groups, such as amino acid, such as organic phosphinic acid, such as an alkylphosphine acid and glycero phosphinic acid, a glycine, and beta-alanine, and a hydrochloride of triethanolamine, etc., two or more sorts may be mixed and you may use.

[0026] This organic undercoat can be prepared by the following approaches. That is, it is the approach of an aluminum plate being immersed in the solution made dissolving the above-mentioned organic compound in organic solvents or those partially aromatic solvents, such as an approach of applied and drying and preparing the solution made dissolving the above-mentioned organic compound in organic solvents or those partially aromatic solvents, such as water or a methanol, ethanol, and a methyl ethyl ketone, on an aluminum plate, water or a methanol, ethanol, and a methyl ethyl ketone, making the above-mentioned compound sticking to it, washing and drying bywater etc. after that, and preparing organic undercoat. By the former approach, the solution of 0.005 – 10% of the weight of the concentration of the above-mentioned organic compound can be applied by various approaches. Moreover,

by the latter approach, the concentration of a solution is 0.05 – 5 % of the weight preferably 0.01 to 20% of the weight, 20–90 degrees C of immersion temperature are 25–50 degrees C preferably, and immersion time amount is 2 seconds – 1 minute preferably for 0.1 to 20 minutes. The solution used for this can also be used in the range of pH 1–12 by acid, such as alkalis, such as ammonia, triethylamine, and a potassium hydroxide, and a hydrochloric acid, a phosphoric acid. Moreover, a yellow color can also be added for tune repeatability amelioration of the photosensitive lithography version. 2 – 200 mg/m² is suitable for the amount of coats of organic undercoat, and it is 5 – 100 mg/m² preferably. If there are few above-mentioned amounts of coats than 2 mg/m², sufficient print durability ability will not be obtained. Moreover, it is the same even if larger than 200 mg/m². Moreover, in order to shorten the time amount of the vacuum suction in the case of the adhesion exposure which used the vacuum printing frame and to prevent baked dotage, a mat layer is prepared in the front face of the positive type photosensitivity constituent layer for the printing versions of this invention. concrete — JP,50-125805,A and JP,57-6582,B — said — 61-28986 The approach of preparing a mat layer which is indicated by each official report of a number, the approach of carrying out thermal melting arrival of the solid-state powder which is indicated by JP,62-62337,B, etc. are mentioned. The pitch diameter of the mat layer used for this invention has desirable 100 micrometers or less, and it is 2–8 micrometers as more desirable range. If a pitch diameter becomes large, a thin line cannot be attached easily, point decrease also of the highlights dot is carried out, and it is not desirable on tone reproduction. In 2 micrometers or less, vacuum adhesion is inadequate, and burns and a pitch diameter produces dotage. 5 – 200 mg/m² is desirable still more desirable, and the coverage of a mat layer is 20 – 150 mg/m². If coverage is larger than this range, it will become the cause of an abrasion, and if smaller than this, vacuum adhesion will serve as imperfection.

[0027] Image exposure and a development stroke are usually given to the positive type photosensitivity printing version created as mentioned above. As the light source of the activity beam of light used for image exposure, there are a mercury-vapor lamp, metal halide, a xenon lamp, a chemical lamp, a carbon arc, etc., for example. As a radiation, there are an electron ray, an X-ray, an ion beam, far infrared rays, etc. Moreover, g line, i line, Deep-UV light, and a high density energy beam (laser beam) are also used. As a laser beam, a helium neon laser, an argon laser, krypton laser, a helium cadmium laser, a KrF excimer laser, etc. are mentioned. The alkali water solution conventionally known as the developer and replenisher of the printing version using

the positive type photosensitivity constituent for the printing versions of this invention can be used. For example, inorganic alkali salt, such as a sodium silicate, this potassium, the 3rd sodium phosphate, this potassium, this ammonium, the 2nd sodium phosphate, this potassium, this ammonium, sodium bicarbonate, this potassium, this ammonium, a sodium carbonate, this potassium, this ammonium, a sodium hydrogencarbonate, this potassium, this ammonium, way acid sodium, this potassium, this ammonium, a sodium hydroxide, this ammonium, this potassium, and this lithium, is mentioned. Moreover, organic alkali chemicals, such as monomethylamine, dimethylamine, a trimethylamine, a monoethyl amine, diethylamine, triethylamine, mono-isopropylamine, disopropylamine, a triisopropyl amine, n butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and a pyridine, are also used. These alkali chemicals are used combining independent or two sorts or more. As a developer especially desirable in these alkali chemicals, they are silicate water solutions, such as a sodium silicate and a potassium silicate. The reason is oxidation silicon which is the component of a silicate. SiO₂ Alkali-metal oxide An alkali-metal silicate which is because accommodation of development nature is attained with the ratio and concentration of M₂O, for example, is indicated by JP,54-62004,A and JP,57-7427,B is used effectively. Furthermore, it is known that a lot of PS plates can be processed, without exchanging the developer in a long duration developing tank by adding a water solution with alkali reinforcement higher than a developer (replenisher) to a developer, in developing negatives using an auto-processor. Also in this invention, this supplement method is applied preferably.

[0028] Various surfactants and organic solvents can be added if needed in order to raise the parent ink nature of acceleration of development nature, control, distribution of development dregs, and the printing version image section to the developer and replenisher which are used for this invention. As a desirable surface active agent, an anion system, a cation system, the Nonion system, and an amphoteric surface active agent are raised. Furthermore, reducing agents, such as sodium salt of inorganic acids, such as hydroquinone, resorcinol, a sulfurous acid, and sulfurous-acid hydro acid, and potassium salt, and also an organic carboxylic acid, a defoaming agent, and a water softener can also be added to the developer and replenisher of this invention if needed. After treatment of the printing version by which the development was carried out using the above-mentioned developer and the replenisher is carried out by the rinse containing rinsing water, a surface active agent, etc., and insensible **** containing gum arabic or a starch derivative. It can use for the after treatment of the

printing version of this invention combining various these processings. In recent years, in platemaking / printing industry, the auto-processor for the printing versions is widely used for rationalization of a platemaking activity, and a standardization. This auto-processor sprays and carries out the development of each processing liquid pumped up with the pump from a spray nozzle, consisting of the development section and the after-treatment section generally, consisting of the equipment, each processing cistern, and spray equipment which convey the printing version, and conveying the printing version [finishing / exposure] horizontally. Moreover, how to make carry out immersion conveyance of the printing version with a guide-among liquid roll etc. into the processing cistern with which processing liquid was filled, and process is also learned recently. It can process in such automatic processing, supplementing each processing liquid with a replenisher according to a throughput, the operating time, etc. Moreover, the so-called disposable mode of processing substantially processed with intact processing liquid is also applicable. the lithography version obtained by such processing is covered over the offset press etc. -- having -- many -- it is used for printing of several sheets.

[0029]

[Example] Although an example explains this invention to a detail below, it is not limited to this.

after carrying out trichlene washing of the aluminum plate (construction material 1050) with an examples [1-3] and an example a-e thickness [of a comparison] of 0.3mm and degreasing, it is grain about this front face using a nylon brush and the pass I water suspension of 400 meshes -- it **(ed) and often washed with water. It etched by being immersed in a sodium-hydroxide water solution for 9 seconds 25 45-degree C%, and after rinsing, it was immersed in the nitric acid for 20 seconds 20 more%, and this plate was rinsed. The amounts of etching on the front face of graining at this time were about 3g/m². Next, it is current density 15 A/dm², using a sulfuric acid as the electrolytic solution for this plate 7%. Rinsing desiccation was carried out after preparing the direct-current anodic oxide film of 3 g/m². The following sensitization liquid (table 1 reference) examples 1-3 and following example a-e of a comparison were applied to this aluminum plate at this degree, desiccation was carried out for 100-degree-C 2 minutes, and the positive type photosensitivity printing versions 1-3 and a-e were obtained. All the coverage after desiccation was 2.4 - 2.5 g/m². After exposing these positive type photosensitivity printing versions from the distance of 70cm by the 30A carbon arc lamp, the 8 time diluent of DP-4 (trade name: Fuji Photo Film, Inc. make) performed automatic development (800U:

based on the auto-processor by Fuji Photo Film, Inc.) for 25-degree-C 40 seconds. The fitness exposure time at this time was made into the point that five steps become clear thoroughly with the gray scale (Fuji Photo Film, Inc. make) of the concentration difference 0.15, and, thereby, was made into the sensibility of the photosensitive printing version. Moreover, the time amount (development admissibility is called below.) which changes from the solid number of stages of the gray scale at the time of 40-second development two steps in 25-degree C vat development with the 8 time diluent of DP-4 was found. The result of the sensibility (exposure time) of these positive type photosensitivity printing versions and development admissibility is shown in a table 2.

[0030]

[A table 1]

Table 1 Sensitization liquid	Example 1
Example 2 The example 3	naphthoquinone
-1, 2-diazido-5- 0.90 0.90 0.90 sulfonic-acid chloride and pyrogallol - (g)	
An ester compound with acetone resin	
Cresol formaldehyde resin 1.70 1.70 1.70	
t-butylphenol-HORUMUARUDEHI 0.05 0.05 0.05 DO resin	
	A naphthoquinone -1, 2-diazido-4- 0.03
0.030.03 sulfonic-acid chloride	Oil blue
#603 0.02 0.020.02	4 and 4'-screw
(4-hydroxy FENI) [0.30] -- RU-cyclohexane carboxylic acid	
	2 and 2'-screw () [4-hydroxy FENI] - 0.30
- RU-4-methylcyclohexane carboxylic acid	
	2 and 2'-screw () [4-hydroxy FENI] --
0.30 RU -3, 6-dimethylcyclohexane carboxylic acid	
	Tetrahydro phthalic anhydride ---
	2, 3, 4-trihydroxy BENZOFE - As - non, -
A condensate with formaldehyde	Gallic
acid ---	A methyl ethyl ketone 8 88
	2-methoxy ethyl acetate 15 15 15
	Table 1 (continuation) sensitization liquid
Example a of a comparison Example b of a	
comparison Example c of a comparison Example d of a comparison The example e of a	
comparison	Naphthoquinone - 1 Two
0.900.70 0.90 0.90 The ester compound of 0.90-diazido-5-sulfonic-acid chloride and	

pyrogallol-acetone resin -----
 Cresol-HORUMUA 2.00 2.20 1.85 1.70 1.90 RUDEHIDO resin
 ----- t-butylphenol 0.05 0.05 0.05 0.05
 0.05-formaldehyde resins ----- Naphthoquinone
 - 1 Two 0.03 0.03 0.03 0.03 diazido-4-sulfonic-acid chloride
 ----- Oil blue #603 0.02 0.02 0.02 0.02 0.02
 ----- a 4 and 4'-screw (4- - - - -
 -hydroxyphenyl)
 - cyclohexane-carboxylic-acid ----- a 2 and
 2'-screw (4- - - - -hydroxyphenyl)
 - 4-methylcyclohexane carboxylic-acid ----- a
 2 and 2'-screw (4- - - - -hydroxyphenyl)
 - 3, 6-dimethylcyclohexane carboxylic acid
 ----- Tetrahydro anhydrous free wheel plate --
 0.15 -- A RU acid ----- 2, 3, 4-TORIHIDO --
 0.30 - The condensate of a ROKISHI benzophenone and formaldehyde
 ----- A gallic acid - - - 0.10
 ----- Methyl ethyl ketone 8 8 8 8 8
 ----- 2-methoxy ECHIRUA 15 15 15 15
 15SETETO ----- [a table 2]
 Table 2 Performance-evaluation table ----- Admiration Whenever
 Development admissibility (exposure time)
 ----- An example 1 55 (second) 7 minutes -----
 An example 2 50 7 minutes ----- An example 3 60 7 minutes
 ----- The example a of a comparison 120 8 minutes The example
 b90 of a comparison 3 minutes Example c of a comparison 80 4 minutes Example d of
 a comparison 85 5 minutes Example e of a comparison 754 minute
 ----- [0031] Although sensibility is rising clearly (the fitness
 exposure time is short) and development admissibility is more slightly [than the
 example a of a comparison] inferior in the examples 1-3 which added the compound
 of the general formula (I) of this invention compared with the example a of a
 comparison as shown in a table 2, it is extent which does not become a practical skill
 top problem. On the other hand, the example b of a comparison which decreased the
 amount of o-quinone diazide compound has large lowering of development
 admissibility, although lifting of sensibility is accepted. Moreover, conventionally,
 although sensibility rises in each well-known additive, development admissibility will

become narrow too. When the printing trial of examples 1-3 and the example a of a comparison without an additive was carried out, the good result which is satisfactory as for other engine performance was obtained.

[0032] Example 4 naphthoquinone -1, 2-diazido-5-sulfonic-acid chloride 0.85g Ester compound cresol formaldehyde resin with m-cresol formaldehyde resin 1.85g 2 and 2'-bis(4-hydroxyphenyl)-3-MECHIRUSHIKU 0.25g ROHEKISAN carboxylic-acid Victoria pure blue BOH 0.01g crystal violet 0.01g 2-(p-methoxy styryl)-4, 6-screw () [TORIKUROROME] 0.03g Chill-s-triazine ethylene dichloride 16g 2-methoxy ethyl acetate The photosensitive coating liquid of the 12g above-mentioned presentation was applied to the aluminum plate which surface roughening was electrochemically carried out and was anodized. The film weight after the desiccation at this time was 2.3 g/m². In this way, the obtained sensitive plate was made the same with an example, and the optimal exposure time and development admissibility were investigated. As a result, the optimal exposure time was 60 seconds, and development admissibility was for 7 minutes. When printed having printing covered [which was obtained as mentioned above] it over the offset press, several many prints with a good image were obtained.

[0033] The following sensitization liquid (table 3 reference) examples 5 and 6 and the example f of a comparison were applied to the aluminum plate used in examples 5 and 6 and the example of comparison f example 1, desiccation was carried out for 100-degree-C 5 minutes, and the positive type photosensitivity printing versions 5 and 6 and the example f of a comparison were acquired. the coverage after desiccation -- all -- 2.3 - 2.4 g/m² it was . Sensibility of these positive type photosensitivity printing versions (exposure time) The same actuation as an example 1 performed development admissibility. The result is shown in a table 4. A table 4 shows that development admissibility is lowering of the range where improvement in sensibility is found as compared with the example f of a comparison, and the photosensitive printing version (examples 5 and 6) of this invention does not become a problem on practical skill.

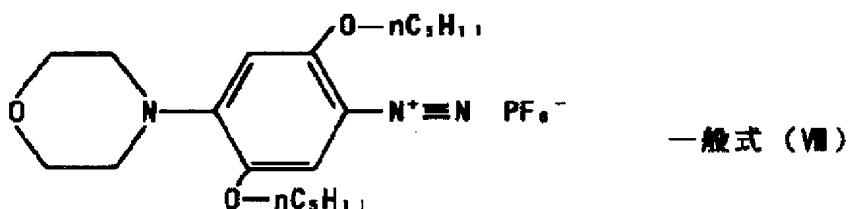
[0034]

[A table 3] Table 3 Sensitization liquid

	実施例 5	実施例 6	比較例 f
下記式(VIII)のジアソニウム塩	0.2 (g)	0.2	0.2
クレゾールーホルムアルデヒド樹脂	1.0	1.0	1.0
オイルブルー# 6 0 3	0.02	0.02	0.02
4,4'-ビス(4-ヒドロキシフェニル)-シクロヘキサンカルボン酸	0.15	---	---
2,2'-ビス(4-ヒドロキシフェニル)-4-	---	0.15	---
メチルシクロヘキサンカルボン酸			
メチルエチルケトン	4	4	4
2-メトキシエチルアセテート	7	7	7

[0035]

[Formula 5]



[0036]

[A table 4]

表4 性能評価表

感度 (露光時間)	現像許容性
実施例 4 4.5秒	7分
実施例 5 5.0秒	7分
比較例 f 7.0秒	8分

[Translation done.]